# Stereochemistry of organic compounds(11) : On the formation of hemiacetals in aldose

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# Stereochemistry of Organic Compounds XI[1)]
# On the Formation of Hemiacetals in Aldose

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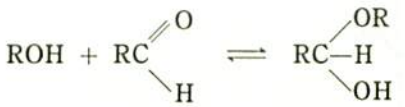
In order to study the behavior of free sugars in different solutions, we have investigated the optical contributions as related to temperature and solvent dependency of tetrose, pentose and hexose. The compounds studied are D-erythrose (Compound I), D-ribose (Compound II) and D-arabinose (Compound III). The solvents we used are water and ethanol at 20°C and 60°C.

The reaction of aliphatic aldehydes to form hemiacetal (1) in alcoholic medium has been confirmed.[2-4)] Compound I is considered to assume a chain



(1)

structure, quite distinct from the common sugars of pyranose structures. As in the case of Forrester's study,[5)] it is anticipated that erythrose in alcoholic medium is mostly present as free aldose at higher temperatures, while the equilibrium moves towards the formation of hemiacetal with decreasing temperatures.

We focused our attention on the production of the new asymmetric carbon. When forming the hemiacetal, then a new asymmetric carbon will have a new partial rotation.

## Results and Discussion

We measured the rotatory dispersion (RD), the circular dichroism (CD) and the ultraviolet absorption (UV) after reaching the equilibrium ($\alpha$-type $\rightleftharpoons$ $\beta$-type) in D-ribose and D-arabinose in order to avoid the effect of mutarotation. In Figures 1 and 2, the RD, CD and UV of Compound I, II and III in water at 20°C and 60°C are given. Compound I exhibits a weak absorption at 276 nm ($\varepsilon$ 16.0)

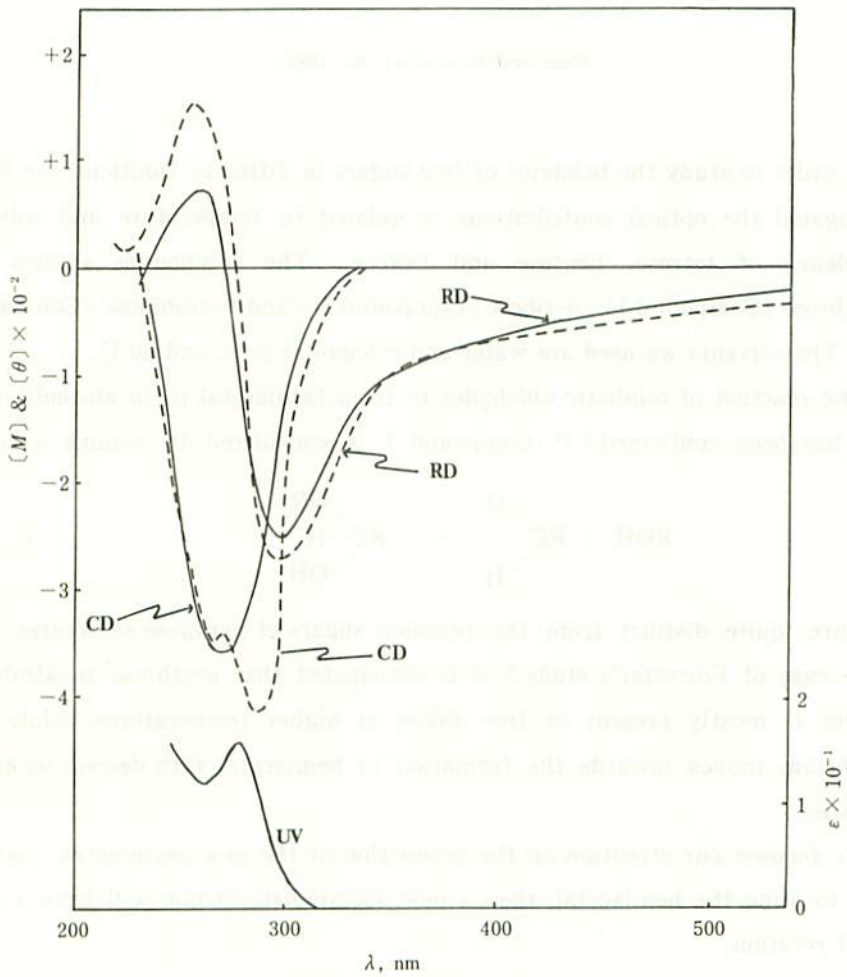



**Fig. 1** CD, RD and UV of Compound I at 20°C (——) and 60°C (- - -) in $H_2O$.

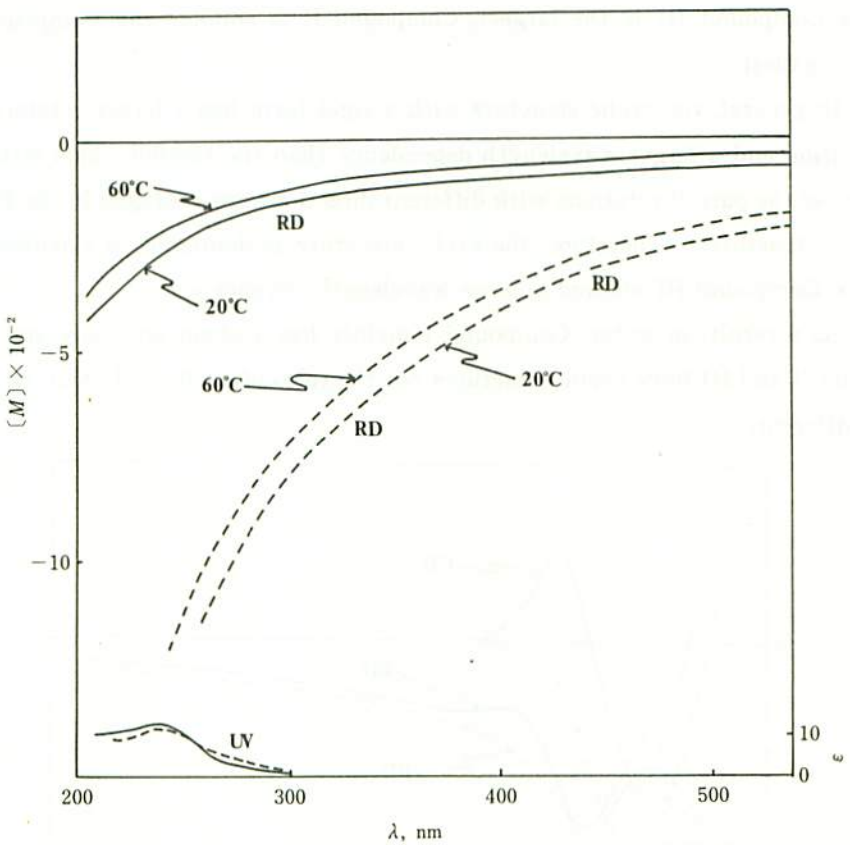



**Fig. 2** RD and UV of Compounds II (——) and III (- - -) at 20°C and 60°C in $H_2O$.

due to the $n \rightarrow \pi^*$ transition of the $\rangle C=O$ group, which corresponds to the negative Cotton effect centered 268 nm at 20°C and 288 nm at 60°C. Meanwhile the CD curves of Compounds II and III do not show any Cotton effects and the curves of these show negative plain curves. Furthermore, the UV curves show weak absorptions around 240 nm due to the $n \rightarrow \pi^*$ transitions. Therefore, in the case of Compounds II and III we observed the following equilibrium,

$$\alpha\text{-form} \rightleftharpoons \text{aldehyde} \rightleftharpoons \beta\text{-form}$$

but, the probability of aldehyde existing is small because Compounds II and III easily assume the cyclic structure carrying no free carbonyl group. The rotational strength, except the wavelength region around the Cotton effect, shows

that Compound III is the largest, Compound II is smaller and Compound I is the smallest.

In general, the cyclic structure with a rigid form has a larger rotatory contribution and a larger wavelength dependency than the flexible chain structure, because the partial rotations with different directions are averaged in the flexible chain structures. Therefore, the cyclic structure is dominant in Compound III since Compound III showed a large wavelength dependency.

As a result, in water, Compound I mainly has a chain structure and Compound II and III have cyclic structures but the ratio of cyclic and chain structure is different.

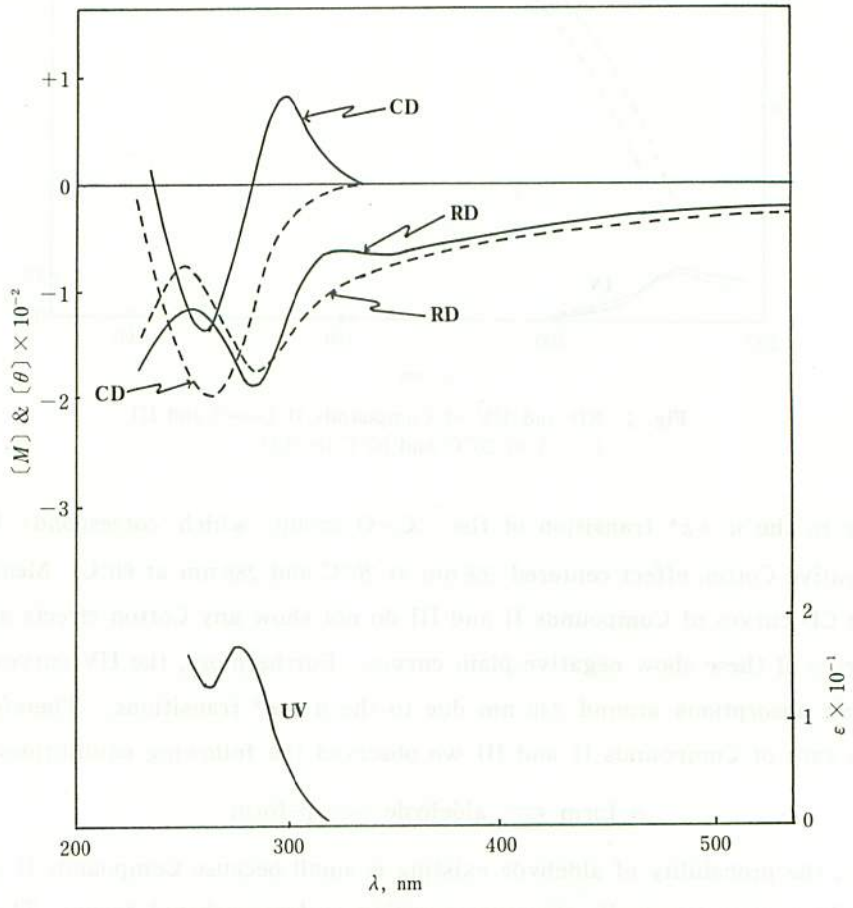



**Fig. 3** CD, RD and UV of Compound I at 20°C (——) and 60°C (- - -) in EtOH.

Next is the information and results of the RD, CD and UV in ethanol. In Figure 3 are given the RD, CD and UV curves of Compound I at 20°C and 60°C. The RD and CD curves in ethanol at 60°C are regarded to be similar in water, although their rotational strengths are different. In case of 20°C, the RD and CD curves are different from the case of 60°C, the RD curve exhibits complex Cotton effects, and the CD curve shows a positive peak at 298 nm and a negative peak at 260 nm. In order to illustrate the difference between the optical contribution in water and in ethanol at 20°C, the RD and CD curves of Compound I are shown in Fig. 4. As is evident in Fig. 4, a negative CD extreme

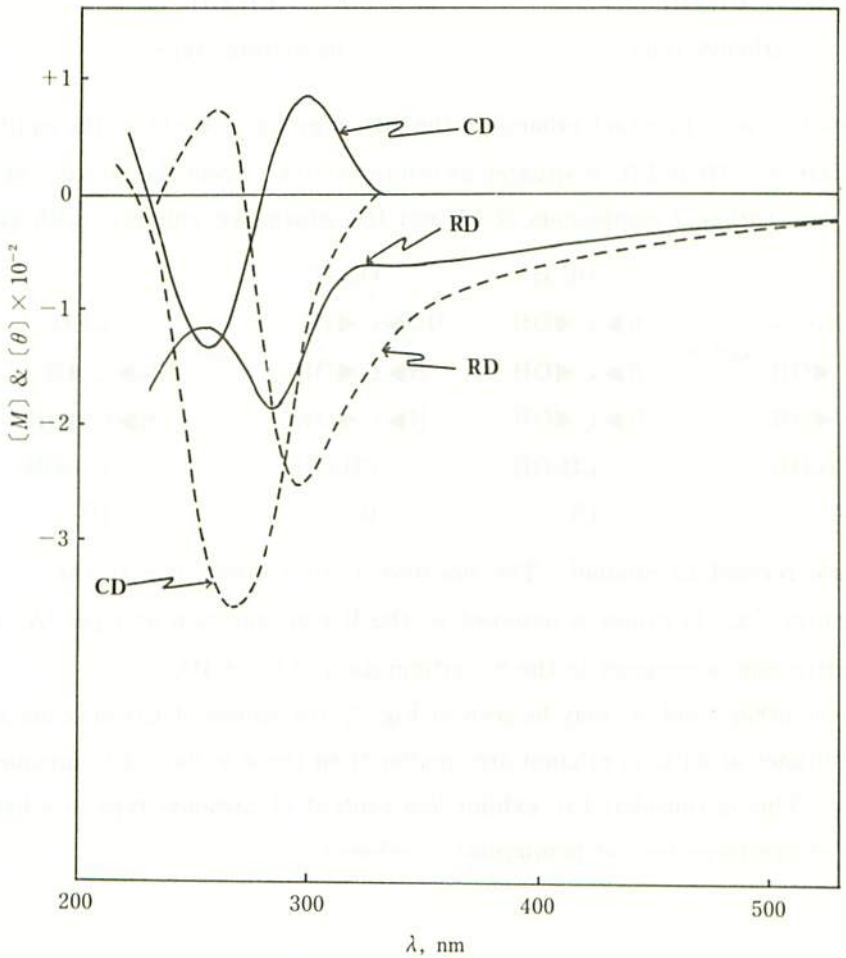
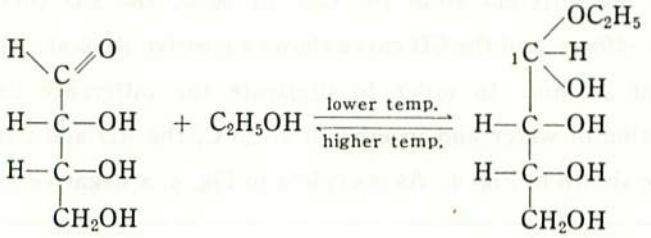



**Fig. 4** CD and RD of Compound I at 20°C in $E_tOH$ (——) and $H_2O$ (- - -).

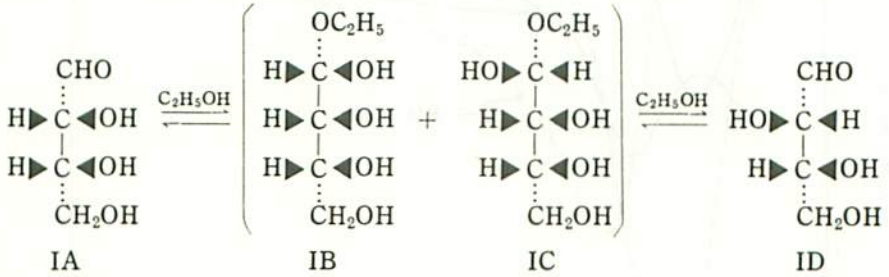
in water appears as two CD extremes, one is positive and the other is negative, in ethanol.

As mentioned above, Compound I in ethanol at lower temperatures is present to some extent as the following hemiacetal type.




carbonyl type　　hemiacetal type

There are two ways to attach ethanol to the planar group, $\rangle C=O$, so the equilibrium mixture of IB and IC is situated as intermediates. From the mixture of IB and IC, two carbonyl compounds of IA and ID, which are epimeric with each



IA　　IB　　IC　　ID

other, are formed in ethanol. The negative Cotton effect due to the $n \rightarrow \pi^*$ transition of $\rangle C=O$ group is assigned to the R-configuration at $C_2$ of IA, and the positive one is assigned to the S-configuration at $C_2$ of ID.

On the other hand, as may be seen in Fig. 5, the values of CD maxima and RD amplitudes at 60°C in ethanol are smaller than those values of Compound I in water. This is considered to exhibit less content of carbonyl type in ethanol because of the formation of hemiacetal in ethanol.

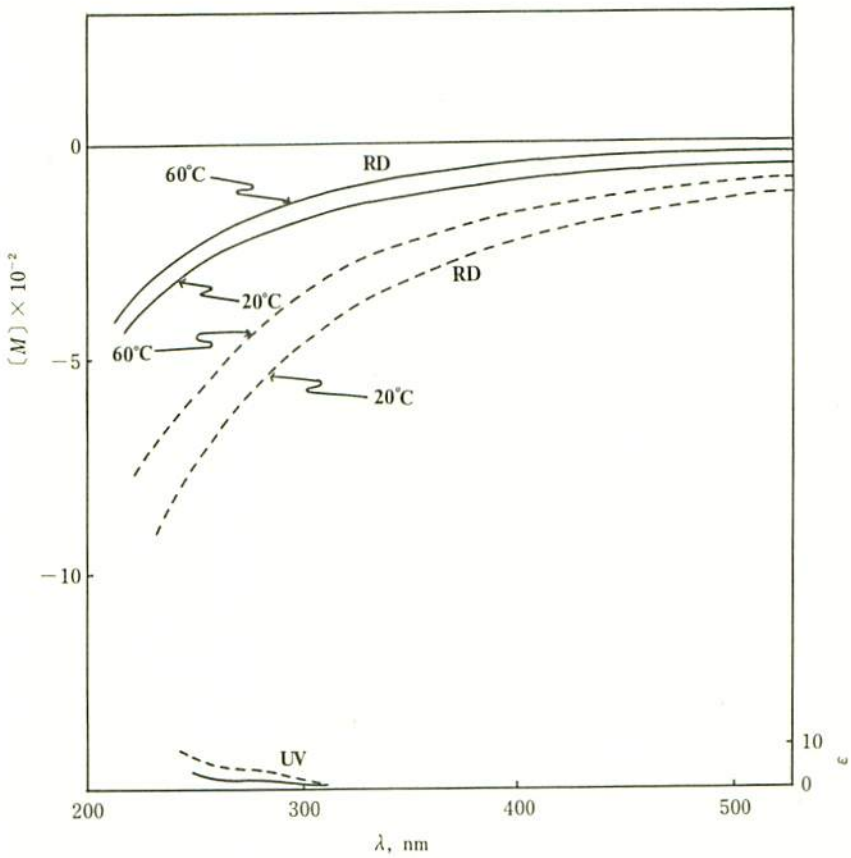



**Fig. 5** RD and UV of Compounds II (——) and III (- - -) in EtOH.

To summarize, the pentose and the hexose easily take the cyclic structure carrying no free carbonyl group, the tetrose exists as the free carbonyl type unepimerized at lower temperatures and, exists as epimers with free carbonyl groups produced via hemiacetal intermediates at elevated temperatures.

## References

1) K. Satsumabayashi and Y. Nishida, This Bulletin, **16**, 89 (1987).
2) A. Ashdown and T. A. Kletz, *Anal. Chem.*, **30**, 1454 (1958).
3) G. B. Sutherland and A. R. Philpotts, *Trans. Faraday Soc.*, **41**, 206 (1945).
4) O. H. Whealer and J. L. Mateos, *Anal. Chem.*, **29**, 538 (1957).
5) J. S. Forrester, *Anal. Chem.*, **32**, 1668 (1960).